

Phase Behaviors of Ammonia / R-125 Mixtures¹

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ABSTRACT

Hydrofluorocarbons (HFCs) are known to have specific intermolecular interactions (hydrogen bonding) as well as large permanent electric dipole moments. The peculiar *VLE* behavior (double azeotropes) observed in R-125/ammonia mixtures led us further to study the phase behaviors of this binary system. The experimental *VLE* (*PTx*) data were measured from 205 to 248 K for six concentrations. Single gaseous phase *PTVx* properties for four concentrations were measured using a constant volume cell: densities of 100, 102, 146, and 224 kg·m⁻³ at temperature ranges of 333 – 385 K. The experimental data, combined with the previously reported data, were analyzed with a cubic equation of state, where non-conventional mixing rules were required in order to fit the experimental *VLE* data satisfactorily. The *VLE* phase behavior is discussed with ammonia mixtures with other compounds. There are strong evidences that some of HFCs and HCFCs form complexes (or even react) with ammonia. The complex formation and *VLE* behavior are elusively related to the number of F atoms and the molecular structure. For R-125/ammonia, it is estimated the enthalpy of complex formation is about -10 kJ·mole⁻¹, which is in concordance with those for hydrogen-bonding and/or charge-transfer complexes reported in the literature.

KEY WORDS: ammonia, azeotrope, equation of state, hydrofluorocarbons, hydrogen bonding, mixing rule, phase equilibria, R-125

1. INTRODUCTION

R-125/R-717 (Pentafluoroethane/Ammonia) binary mixtures show double azeotropy [1], and have been proposed for applications as alternative refrigerants [2]. However, no experimental *VLE* (vapor-liquid-equilibria) data below 254 K have been reported, ever since. Another shortage of this binary system is that there is no single *PVT_x* datum of the gaseous phase. Therefore, we have conducted the present study, in order to obtain more experimental data and to understand the peculiar phase behavior of R-125/ammonia mixtures.

First, brief descriptions of the experimental method are given, together with observed *VLE* (*PT_x*) data and single phase *PVT_x* data. Then, the experimental data are analyzed with the same cubic EOS (equation of state) as those used in a report for R-32/R-125 mixtures [3]. In this work, however, a special mixing rule for modeling the curious intermolecular interactions has been introduced. Next, the *VLE* phase behavior of this system is studied over a wide range of temperatures. The curious shapes of bubble point pressures are compared with those in other ammonia binary systems. By comparing the excess Gibbs free energies of these mixtures, the enthalpy of complex formation in R-125/ammonia mixtures is derived. Then, concluding remarks follow.

2. EXPERIMENTAL

Low temperature *VLE* experiments were performed with a glass cell, which was placed in a transparent Dewar vessel filled with n-pentane. Temperatures were controlled by pumping liquid nitrogen through a heat exchanger installed in the thermostatic liquid pentane. The accuracy in the temperature measurement with a platinum resistance thermometer was within 0.03 K. Saturated vapor pressures were measured with a

hydrostatic manometer with the aid of a cathetometer; the error in the pressure measurement, without counting systematic errors, was not more than 120 Pa. The purity of the sample used was 99.9 % and 99.8 % for R-125 and ammonia, respectively. The estimated error in the mixture concentration did not exceed 0.003 %. More detailed descriptions and experimental procedures are given elsewhere [4.]. Mixtures for six different compositions were investigated in the temperature range of 205 - 248 K. The experimental data are listed in Table 1.

Single gaseous phase PVT_x data were obtained with a constant volume sample cell, which was installed in a temperature-controlled thermostatic bath. Pressure measurements were made with a weight-and-piston manometer through a diaphragm separator. Mixtures of four different compositions were studied with densities of 100.2, 101.8, 145.7, and 223.9 kg•m⁻³ at the temperature range of 333 - 385 K. The experimental results are shown in Table 2.

3. ANALYSES AND RESULTS

In the previous study of R-125/R717 VLE [1], a modified Peng-Robinson EOS was adopted to reproduce the experimental data with sufficient accuracy. However, the binary interaction parameters were determined separately for each isothermal PT_x data set. Here, we have adopted a simple cubic EOS, which was applied for the R-32/125 binary system [3], and correlated the data consistently over all temperature ranges :

$$P = \frac{RT}{v + c - b} - \frac{a}{(v + c)^2} \quad (1)$$

With $V = v + c$, this becomes the familiar van der Waals form;

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \quad (2)$$

Here, c is a constant for each pure compound, and since the differential $dV = dv$, all thermodynamic relations can be constructed by the van der Waals's equation (2). For a general N -component system, the three parameters a , b , and c are modeled by:

$$a = \sum_{i,j=1}^N \sqrt{a_i a_j} (1 - k_{ij}) x_i x_j \quad (3)$$

$$a_i = a_{ci} \alpha_i(T), \quad a_{ci} = \frac{27}{64} \frac{(RT_{ci})^2}{P_{ci}} \quad (4)$$

$$\alpha_i(T) = \sum_{k=0}^{\leq 3} \beta_{ik} \left(\frac{1}{T_r} - T_r \right)^k, \quad T_r = \frac{T}{T_{ci}} \quad (5)$$

$$k_{ij} = \frac{L_{ij} L_{ji} (x_i + x_j)}{L_{ji} x_i + L_{ij} x_j} (1 + B_{ij} T + C_{ij} T^2), \quad k_{ii} = 0, \quad B_{ji} = B_{ij}, \quad C_{ji} = C_{ij} \quad (6)$$

$$b = \sum_{i,j=1}^N \frac{b_i + b_j}{2} (1 - m_{ij}) x_i x_j, \quad m_{ji} = m_{ij}, \quad m_{ii} = 0, \quad \text{and} \quad b_i = \frac{1}{8} \frac{RT_{ci}}{P_{ci}} \quad (7)$$

$$c = \sum_{i=1}^N c_i x_i \quad (8)$$

It should be mentioned that the mixing rule Eq. (6) adopted here is different from that in Ref. [3], since the present binary system cannot be correlated with the usual mixing rule used in Ref. [3]. With $L_{ij} = L_{ji}$ in Eq. (6), however, this is reduced to the usual quadratic mixing rule. This type of mixing rule has been successfully applied for refrigerant-lubricant *VLE* data [5, 6].

The EOS coefficients for pure R-125 are taken from the previous study [3], and those for pure R-717 have been determined using a highly accurate EOS correlation in the literature [7]. The results are given in Table 3 for the *VLE* two phase (*VLE*-EOS) and

the single phase (*Vapor*-EOS) regions. The binary interaction parameters for the *VLE*-EOS of Eq. (6) were determined from the present low temperature data combined with the previously reported data [1]. The binary interaction parameters for the *Vapor*-EOS were obtained using the present data in Table 2. The determined parameters are listed in Table 4, and Figure 1 shows deviation plots of the present data analyses. It may be worth to mention that the gaseous phase data were well correlated with $L_{ij} = L_{ji}$ in Eq. (6) (the usual mixing rule), while the *VLE* data required non-symmetric L_{ij} .

4. DISCUSSIONS OF PHASE BEHAVIOIRS

4.1. Multiple Azeotropy

As can be seen in Fig. 2, the binary system shows double azeotropes (maximum and minimum) at $T = 323.05$ K. Calculations with the present model predict that the double azeotropy becomes a saddle point azeotrope around 298 K and below this temperature no true azeotropy occurs, as seen in Fig. 2. The double azeotropy continues up to the *VLE* critical line, the minimum azeotrope first meets the critical line and ends, and a single maximum azeotropy continues up to the critical line.

The first and well-documented double azeotropy in homogeneous mixtures is a binary system of perfluorobenzene and benzene [8], where it is believed to form equimolar intermolecular complexes in the liquid phase.

4.2. Low Temperature Regions

Mixtures with ammonia-rich concentrations become more non-ideal with the decrease in temperature; see Fig. 2. It suggests that at sufficiently low temperatures the system might form two separated liquids (Vapor-liquid-liquid equilibria: *VLLE*). In fact, a miscibility gap of *VLLE* has been calculated in low temperature regions, and is shown

in Fig. 3, together with an isothermal PT_{xy} diagram. The UCST (Upper Critical Solution Temperature) is about 198 K at the ammonia concentration of about 89 mole %. This heterogeneous type is called a heterogeneous azeotrope of the *second* kind.

4.3. VLE Critical Points

Critical loci of temperature, pressure and density have been calculated as a function of composition, using the same method as described in Ref. [3], and are shown in Fig. 4. Although the *VLE* behavior exhibits curious double and/or saddle-point azeotropes as discussed above, the critical loci of this system are rather ordinary and simple, although the mixture critical parameters significantly deviate from the Kay's rule (linear dependence on mole fractions).

4.4. Comparisons with Other Ammonia Mixtures

Few selected examples of other ammonia binary systems are illustrated with isothermal PT_{xy} diagrams in Fig. 5: (a) R-134a ($\text{CH}_2\text{F}-\text{CF}_3$) [2], (b) R-143a (CH_3-CF_3) [2], (c) R-134 ($\text{CHF}_2-\text{CHF}_2$) [2], (d) R-227ea ($\text{CF}_3-\text{CHF}-\text{CF}_3$) [2], (e) R-22 (CHClF_2) [9], and (f) R-12 (CCl_2F_2) [9]. The calculated curves are based on the same EOS model as used at the present study. Two characteristic shapes of the bubble point pressure can be observed: (1) usual maximum pressure azeotrope, including heterogeneous case, and (2) positive and negative deviations from the Raoult's law, including double azeotrope. R-125/ammonia system belongs to the second case (2). Among other ammonia mixtures not shown here, R-32 (CH_2F_2) [2], R-142b ($\text{CH}_3-\text{CClF}_2$) [9], R-114 ($\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$) [9], and n-butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$) [10] belong to the first case (1), while R-23 (CHF_3) and R-124 ($\text{CHClF}-\text{CF}_3$) [9] belong to the case (2). The case (2) is indicative for the existence of specific intermolecular interaction such as hydrogen bonding. In the case of

R-22, it is known to be chemically reactive with ammonia, forming ammonium fluoride. Whether the system belongs to the case (1) or the case (2) is quite elusive and puzzling, when we look at the difference of chemical structures and/or molecular polarities.

4.5. Excess Free Energy and Complex Formation

The excess Gibbs (G) free energy of binary mixtures gives more quantitative aspects for characterizing the type of mixtures: cases (1) and (2) mentioned in the section 4.4. Fig. 6 shows the excess G energy of R-125/ammonia (case (2)) and R-12, R-114, and n-butane/ammonia (case(1)), calculated at $T = 273.15$ K with the present EOS. Gaw and Swinton [8] estimated the enthalpy of formation of the complex, Δh_{comp} , for perfluorobenzene/benzene solutions using the excess G functions and the ideal associated solution theory: $\Delta h_{comp} = -9.7 \text{ kJ}\cdot\text{mol}^{-1}$. Here, we follow their method to estimate Δh_{comp} for R-125/ammonia mixtures, using a reference mixture of R-12, R-114, or n-butane/ammonia. The excess free energy of complex formation is given by:

$$G(\text{complex formation}) = G(\text{R-125/ammonia}) - G(\text{reference mixture}). \quad (9)$$

The equilibrium constant for the complex formation, K_{comp} , is fitted in the following form:

$$K_{comp} = K_0 \exp(-\Delta h_{comp} / RT), \quad (10)$$

K_0 and Δh_{comp} were determined at the equimolar mixture composition in Eq. (9) and using two temperatures of 273.15 and 248.15 K: $\Delta h_{comp} = -10.5$ (from the R-12 mixture reference), -10.9 (from R-114), and -9.1 (from n-butane) $\text{kJ}\cdot\text{mol}^{-1}$, respectively. Figure 7 shows the excess free energy of complex formation of Eq. (9) at 323.15 K (heavy line) and the predicted excess energy of the ideal associated solution theory with Eq. (10) (thin

line). Both curves are in reasonable agreement. The reference mixture is the n-butane/ammonia system, but similar plots were obtained with the R-12 and R-114 reference mixtures.

5. CONCLUSIONS

The curious *VLE* phase behavior of the R-125/ammonia system was well correlated using a simple cubic EOS with a non-quadratic mixing rule. The unusual shapes of the bubble point pressure are due to the intermolecular complex formation in the liquid phase; the enthalpy of the complex formation is estimated to be 9 - 10 kJ·mol⁻¹. Single phase *PVT_x* data were well correlated with the usual quadratic-mixing rule, indicating that no significant molecular association exists in the gas phase.

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Table 1. PTx data of VLE of R-125/Ammonia mixtures(*).

$x_1 = 0.0708$		$x_1 = 0.2169$		$x_1 = 0.4749$		$x_1 = 0.8521$		$x_1 = 0.9507$	
T, K	P, bar	T, K	P, bar	T, K	P, bar	T, K	P, bar	T, K	P, bar
206.32	0.22965	212.18	0.33647	205.21	0.2349	210.98	0.42671	206.3	0.35261
207.41	0.24497	213.34	0.36178	206.32	0.25222	215.74	0.57017	207.3	0.37526
208.6	0.26229	214.21	0.38109	207.31	0.26887	217.28	0.61949	208.61	0.40457
210.03	0.28494	215.66	0.41573	210.03	0.31883	218.62	0.66438	210.01	0.43896
211.19	0.30359	217.21	0.45303	211.06	0.34002	220.09	0.71648	211.06	0.46627
		218.57	0.49033	212.19	0.36306	221.45	0.76909	212.18	0.49789
$x_1 = 0.5133$		220.06	0.53524	213.34	0.39037	222.55	0.81279	213.37	0.53339
T, K	P, bar	221.48	0.57653	214.25	0.41036	223.76	0.86382	214.27	0.56061
213.35	0.3966	222.62	0.61504	215.66	0.44033	224.9	0.91487	215.72	0.60626
214.3	0.42457	223.76	0.65261	217.21	0.48895	226.05	0.96749	217.26	0.6589
215.63	0.45921	224.92	0.69416	218.64	0.53106	227.29	1.02741	218.64	0.70801
217.12	0.49918	226.07	0.73766	220.07	0.57522	228.49	1.08804	220.07	0.76343
218.58	0.54247	227.31	0.78752	221.46	0.62098	229.69	1.15248	221.45	0.81869
220.11	0.58804	228.46	0.8368	222.53	0.65816	230.81	1.21561	222.53	0.86484
221.57	0.63614	229.71	0.8894	223.73	0.70163	232.02	1.28674	223.73	0.91878
222.53	0.67098	230.82	0.94273	225.00	0.75219	233.06	1.35055	224.92	0.97368
223.74	0.71353	232.04	1.00248	226.06	0.79496	234.06	1.41149	226.07	1.02684
225.04	0.76965	232.91	1.04531	227.32	0.84892	235.12	1.48316	227.31	1.0927
226.09	0.81175	235.11	1.16851	228.45	0.89936	236.02	1.54521	230.83	1.29294
227.31	0.86439	236.05	1.22571	229.72	0.95999	237.09	1.62100	232.04	1.36752
230.71	1.02123	237.12	1.29237	230.81	1.0089	238.1	1.68161	233.1	1.43072
232.02	1.09209	238.13	1.35601	232.27	1.08636	239.13	1.77087	234.07	1.50040
233.05	1.14848	239.14	1.42056	233.07	1.13353	240.06	1.84414	235.09	1.57214
234.06	1.20860	240.08	1.48657	235.13	1.25373	241.02	1.92141	236.04	1.64058
235.11	1.27164	241.01	1.55483	236.08	1.3124	242.03	2.00400	237.1	1.71851
236.04	1.32838	242.00	1.6241	237.15	1.38168	243.02	2.08993	238.11	1.78961
237.09	1.39692	242.99	1.70337	238.16	1.44868	243.88	2.16653	239.12	1.87354
238.09	1.46155	243.85	1.77264	239.13	1.51372			240.07	1.95014
239.05	1.53121	244.81	1.8652	240.06	1.58285			241.02	2.03556
240.04	1.60248	245.61	1.91519	241.04	1.65478			242.02	2.11083
241.01	1.67430	246.53	1.99778	242.01	1.73205			243.02	2.20609
242.02	1.75156	247.39	2.07439	243.00	1.80932			243.88	2.28535
242.99	1.82950	248.00	2.13100	243.86	1.8786				
243.86	1.90010			244.75	1.95495				
244.75	1.97471			245.61	2.02755				
245.62	2.04997			246.54	2.11148				
246.54	2.13457			247.28	2.17942				

(*) x_1 = mole fraction of R-125.

Table 2. Isochoric $PTVx$ data of superheated gases of R-125/Ammonia mixtures(*).

$x_1 = 0.6213$ $D = 145.687 \text{ kg}\cdot\text{m}^{-3}$		$x_1 = 0.4013$ $D = 100.165 \text{ kg}\cdot\text{m}^{-3}$		$x_1 = 0.6370$ $D = 101.786 \text{ kg}\cdot\text{m}^{-3}$		$x_1 = 0.7771$ $D = 223.92 \text{ kg}\cdot\text{m}^{-3}$	
$T, \text{ K}$	$P, \text{ bar}$	$T, \text{ K}$	$P, \text{ bar}$	$T, \text{ K}$	$P, \text{ bar}$	$T, \text{ K}$	$P, \text{ bar}$
333.365	28.0282	353.189	25.8906	333.294	30.698	333.294	30.698
343.163	30.5967	367.9	27.9026	343.181	34.1752	343.181	34.1752
353.201	33.1449	367.912	27.8906	353.142	37.537	353.142	37.537
367.862	36.7581	374.696	28.9421	367.866	42.3449	367.866	42.3449
374.663	38.418	385.02	30.622	374.655	44.5304	374.655	44.5304
385.051	40.9109						

(*) x_1 = mole fraction of R-125.

Table 3. Molecular constants used in the present study.

Name	Mw	T_c	P_c	β_0	β_1	β_2	β_3	c
	$\text{g}\cdot\text{mol}^{-1}$	[K]	[kPa]					$[\text{m}^3\cdot\text{kg}^{-1}]$
R-125 ^(a)	120.02	339.40	3631	1.00172	.50400	-.062988	.010437	0
R-717 ^(a)	17.03	405.40	11333	1.00340	.46887	-.057983	-.000763	0
R-125 ^(b)	120.02	339.40	3631	1.00502	.52751	.493060	-.41335	3.0960×10^{-4}
R-717 ^(b)	17.03	405.40	11333	1.00340	.46887	-.057983	-.000763	1.4548×10^{-3}

^(a) Constants for two phase *VLE*-EOS. ^(b) Constants for single phase *Vapor*-EOS.

Table 4. Binary interaction parameters for R-125 (1) / R-717 (2) system.

(1) / (2) System	L_{12}	L_{21}	$m_{12, 21}$	$B_{12, 21}$	$C_{12, 21}$
<i>VLE</i> -EOS ^(a)	-.44345	-.54174	-.20897	-1.5198×10^{-3}	0.0
<i>Vapor</i> -EOS ^(b)	6.6566	L_{12}	-1.7608	-.039665	5.0372×10^{-5}
^{(a), (b)} Refer to Table 1.					

FIGURE CAPTIONS

Figure 1. Deviation plots of calculated and observed data for the R-125/ammonia binary system. (a) Two phase $VLE-PTx$ deviations in the bubble point pressure. (b) Single gaseous phase $PVTx$ deviations: solid circles: pressure, and open circles: density.

Figure 2. $PTxy$ diagrams of three isothermal bubble/dew point pressures for the R-125/ammonia system. Symbols: experimental data points [1]. Lines: calculated with the present EOS.

Figure 3. Phase behaviors at low temperature regions of the R-125/ammonia system. (a) Liquid-liquid separation gap (VLL E). (b) Isothermal $PTxy$ diagram at $T = 188.15$ K.

Figure 4. Critical loci of the R-125/ammonia system. (a) Critical temperature, (b) critical pressure, and (c) critical density as a function of ammonia mole %.

Figure 5. Comparisons of isothermal $PTxy$ diagrams for ammonia binary mixtures. Symbols: observed data [2, 9]. Lines: calculated with the present EOS. (a) R-134a mixture at $T = 263.15$ K, (b) R-143a at $T = 276.38$ K, (c) R-134 at $T = 263.15$ K, (d) R-227ea at $T = 276.38$ K, (e) R-22 at $T = 288.15$ K, and (f) R-12 at $T = 276.25$ K.

Figure 6. The excess Gibbs free energy at $T = 273.15$ K for ammonia mixtures with R-125, R-12, R-114, and n-butane.

Figure 7. The excess Gibbs free energy of complex formation for the R-125/ammonia system at T of 323.15 K. Heavy lines: Eq. (9) with the n-butane reference mixture. Thin lines: calculated by the ideal associated solution theory: see Text.













